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Environment, Safety, and Health

Volume II

Part 14: Chemical

14.6
The Safe Handling of Fluorine

(Formerly H&SM S21.12)

Recommended for approval by the ES&H Working Group

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New document or new requirements

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14.6

The Safe Handling of Fluorine*

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* **Minor revision**

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The Safe Handling of Fluorine

1.0 Introduction

This document describes the common hazards associated with fluorine and provides the engineered and administrative controls and personal protective equipment requirements for safe use of the material. The document is organized according to the process that workers should follow to safely handle fluorine at LLNL. This includes obtaining information on the chemical and physical hazards of fluorine, designing fluorine systems with appropriate engineered controls, and understanding administrative procedures for purchasing and safely using fluorine, as well as procedures for maintaining fluorine systems.

The provisions of this document apply to pure fluorine, mixtures of fluorine in other gases and oxidizing fluorides such as XeF_6, ClF, ClF_3, ClF_5, and other halogenated fluorides unless otherwise specified. Other reactive fluorides that are *not* vigorous oxidizers (i.e., HF, BF_3, WF_6, and NF_3) are not covered in this document.

2.0 Hazards

2.1 Chemical Hazards

Fluorine is a highly toxic and corrosive pale yellow gas whose sharp, penetrating odor is similar to that of a high concentration of ozone. The most powerful oxidizing element known, fluorine (a halogen) reacts violently with practically all organic and inorganic substances, except metal fluorides in their highest valence state, and a few pure and completely fluorinated organic compounds. However, even these few pure and fluorinated organic compounds may burn in a fluorine atmosphere if they are contaminated with a combustible material or are subjected to high flow rates of fluorine. It was previously thought that noble gases were chemically nonreactive with fluorine. However, this is not the case for fluoro-derivatives of Krypton (KrF_2), Xenon (XeF_2, XeF_4, XeF_6) and Radon. (The chemical properties of fluorine are given in Table 1.)

Hydrogen and fluorine combine with extreme violence, forming hydrogen fluoride. Moreover, it reacts with other halogen gases to form such compounds as ClF, ClF_3, and BrF_3. Although oxygen does not ordinarily react with fluorine, two oxygen fluorides, OF_2 and O_2F_2 were synthesized. The extreme reactivity of fluorine demands that you properly clean and passivate a fluorine system prior to using fluorine in that system. *An explosion and fire may result if proper procedures are not followed.*

Table 1. Chemical properties of fluorine.

Chemical symbol:	F_2
Molecular weight (grams):	38
Cylinder pressure at 21°C	2.0-MPa gauge (300 psig)
Specific volume at 21°C and 1 atm	0.634 m^3/kg (10.2 ft^3/lb)
Specific gravity at 0°C (32°F) and 1 atm	1.696 (air = 1)

2.2 Health Hazards

Inhalation of fluorine gas causes nose and throat irritation, respiratory tract and lung injury, unconsciousness, and even death. If fluorine makes contact with the skin or eyes, burns may result. These burns are caused by heat produced when fluorine or hydrogen fluoride (the result of fluorine reacting with moisture in the air) reacts with the moisture on the skin. Moreover, fluoride ions can penetrate deeply to the bone, replacing the hydroxide ions in the bone to produce injury.

Pain from injuries associated with fluorine exposures is often delayed especially if the fluorine is diluted. Therefore, if you even suspect you may have been exposed, rinse your skin and eyes with large amounts of water; continue rinsing for 20 min. Get immediate medical treatment. Appendix A describes the proper emergency procedures to be followed in the event of exposure to fluorine.

Hygienic Standards. The Occupational Safety and Health Administration (OSHA) allowable limit for an 8-h time-weighted average exposure to fluorine in a 40-h workweek is 0.1 parts per million (ppm). Fluorine gas is so irritating that humans will not tolerate excessive exposures to it. In one incident, brief inhalation of a concentration of 25 ppm caused acute toxic effects in humans. In a study on mice, the lethal concentration for 50% of the mice after 60 min of exposure was 150 ppm. Direct skin exposure to pure fluorine can cause severe burns in 0.2 sec, and an exposure for as long as 0.6 sec can result in thermal flash burns comparable to those produced by an oxyacetylene flame.

3.0 Controls

Because fluorine is a controlled item, the Responsible Individual shall contact the environment, safety, and health (ES&H) Team when operations require its use or the use of its inert gas mixtures. An Integration Work Sheet (IWS), Operational Safety Plan (OSP), and an engineering safety note (ESN) are required prior to beginning each operation involving fluorine. Prior to using or purchasing fluorine, the ES&H Team shall review the safety controls outlined in these documents to determine their adequacy.

Treat mixtures of fluorine and inert gases with the same care as pure fluorine unless otherwise noted in this document or unless individual exceptions have been approved by the area ES&H Team. Document any exceptions in the operation's OSP and in an ESN.

Although fluorine is extremely hazardous, it can be handled safely if the proper precautions are taken. Only trained and competent personnel are permitted to handle fluorine; therefore, the worker should be familiar with the contents of this document, the material safety data sheet (MSDS) for the material, which is available from the supplier, and the OSP and ESN associated with each operation.

3.1 Engineered Controls

An ESN shall be prepared and attached to or referenced in the OSP for all toxic or corrosive gas systems, including fluorine systems. Whenever a change is made to a system, a new or revised ESN is required. Direct any questions regarding ESNs to the pressure safety manager or the area ES&H Team.

The engineered controls prescribed below shall be established to preclude the release of fluorine into the work area.

3.1.1 Isolation

Closed systems, constructed to prevent the escape of gas into work areas, shall be used for all fluorine operations within a building.

3.1.2 Gas Storage Cabinets

All cylinders or containers in use (or ready-to-use status) shall be kept in ventilated gas storage cabinets. Cylinders shall be moved with their caps on until they have been put into and secured in a gas storage cabinet. Gas storage cabinets are commercially available for cylinders in ready-to-use condition. These were developed for the semiconductor industry and can be used without modification for fluorine/inert gas mixtures containing <5% fluorine. (10% fluorine/inert gas mixtures can be used to passivate these systems.)

Gas storage cabinets shall have the following features:

- 18 gauge or thicker steel walls (minimum required by Uniform Fire Code Article 80) for fluorine/inert-gas mixtures containing ≤10% fluorine.
- The smallest doors consistent with safe cylinder handling. The doors shall be self-closing and need louvers so the cabinet will be under flowing suction ventilation at all times (see the next item for air flow specifications).

- Self-closing and self-latching windows to make all routine valve adjustments other than those needed to remove old cylinders and install new ones. Air flow needs to be sufficient to maintain an inflow of air at an average velocity of 200 feet per minute (fpm) and never less than 150 fpm anywhere in the plane of the fully opened window. Test smoke released in the window plane shall never flow outward.
- Toxic gas detectors shall be installed inside the cabinet.
- Cylinders shall be rigidly clamped so that opening the supply valve will not cause torque to be transmitted to the regulator manifold (it has been found to cause leaks). Cabinets used for pure fluorine, inert gas mixtures containing >10% fluorine, other gas mixtures, and oxidizing fluorides should have bare-finish stainless steel walls. Such cabinets also need the following:
    - — Barricades to protect the operator.
    - — Valve handles that protrude through the cabinet wall to minimize the times when an operator opens the cabinet door or window and reaches inside. Air velocities through the holes shall be 500 fpm or more.

3.1.3 Delivery Hardware

Delivery pipes and tubes shall be of all-welded construction or be double walled. The outer tubing shall be under suction ventilation and be continuously monitored for gas leakage. All non-welded joints and fittings shall be in enclosures that are under suction ventilation and monitored for gas leakage. The materials in all-welded lines and the inner tubes of double-walled lines shall be made of compatible materials.

3.1.4 Compatible Materials

Compatible materials shall be used. These are summarized in Appendix B for fluorine and fluorine/inert gas mixtures. Contact the material vendor for guidance about compatible materials for the material, temperature, and pressure you will use. Additional guidance is available from the area ES&H Team.

At room temperature, fluorine reacts slowly with many metals; this often results in the formation of a metal fluoride film that retards fluorine's effect on brass, iron, aluminum, magnesium, and copper. Hence, these metals are quite satisfactory for handling fluorine at room temperature. However, at higher temperatures, you must consult the manufacturer regarding the adequacy of the material to be used. For example, nickel and Monel, which is a nickel-copper alloy, are more resistant to corrosion from fIuorine at higher temperatures.

3.1.5 Passivation of Equipment

All equipment used in fluorine operations shall be thoroughly cleaned, degreased, dried, and passivated. *Never use pure fluorine to passivate fluorine equipment or systems.*

Several procedures can be used for passivation. See Appendix C for examples of cleaning and passivation procedures. The type of procedure used will depend on the system to be installed. Contact the area ES&H Team or the Industrial Hygiene technical leader of the Hazards Control Department for information on procedures.

The passivation procedure shall be described in the OSP for each operation. A passivation procedure checklist unique to each operation is desirable.

All systems shall be flow tested ("dry-run") with dry, inert gas before passivation of the assembled system begins if such testing is feasible.

3.1.6 Discharging Fluorine or Fluorine-Like Materials to the Atmosphere

NEPA/CEQA requirements mandate discharging fluorine, any fluorine mixture, or reactive fluoride to the atmosphere in a controlled manner. See Document 12.4, "Work Enclosures and Local Exhaust Systems for Toxic and Radioactive Materials," in the *ES&H Manual* for further details about how to plan atmospheric discharge controls. The ES&H Team will specify the controls needed. Possible controls include

- Rock salt beds. These are useful for concentrated streams. The fluorine displaces the chlorine, so a chlorine remover is needed just downstream. Chlorine is less reactive and somewhat less toxic.
- Caustic scrubbing followed by precipitation for large gas streams.
- Tall stacks for emergency releases. *Tall stacks are used only for discharging unplanned releases or when other controls for planned releases are not practical!* Use the cylinder leak time specified by the vendor, if possible, or assume a cylinder filled with liquefied gas voids in 30 min and a cylinder containing gas only will void in 5 min when planning for emergency releases.
- Cylinder size limits. Cylinder size limits can be used to reduce the height of a stack needed for emergency releases.

3.1.7 Purging

Any equipment that contained fluorine shall be thoroughly purged with dry, inert gas (such as nitrogen) and evacuated at least once before opening or refilling it. Purging by a sequential evacuation and inert gas backfill is preferred; backfill locations need to be as close to the fluorine/fluoride source as possible. Automated purge controllers should be used whenever possible for sequential evacuation/backfill purging to reduce the risk of human error during this tedious but critical process.

3.1.8 Design Precautions for Fluorine Systems

Pipes and Fittings. Weld the pipes and fittings of lines that are not to be dismantled. Socket-weld fittings are preferable to butt-weld fittings because they are easier to keep free of slag and foreign matter during joining. However, butt-weld fittings are acceptable if shielded arc techniques are used.

Where welding is impractical, use threaded joints or tube fittings, as long as these fittings are contained in an exhaust ventilation enclosure. All pipe joints should be made up using TFE (Teflon) tape and Fluorolube to prevent leaks and galling. Fluorolube is also recommended for straight thread joints to prevent galling. Parker Aircraft, Swagelok or Cajon fittings (or equivalent) may be used where small connections in the system are broken frequently.

Pressure Regulators. Regulators shall be used on a high-pressure fluorine source to facilitate the safe handling of pressure. Do not use a double-valving system alone to control pressure.

The Instrument Shop will not supply a fluorine regulator unless you present the appropriate ESN or authorization from the pressure safety manager. Ensure that all regulators are inspected and pressure tested by the Instrument Shop and are labeled with the LLNL pressure-tested label shown in Document 18.2, "Pressure Vessel and System Design," in the *ES&H Manual*.

Pressure-Relief Protection. For low-pressure work (3 psi or less), blow-out traps, similar to laboratory test tubes, are recommended to warn of blocked lines or vessels when spring-loaded valves or rupture disks are not available. These traps are filled with chlorotrifluoroethylene (Kel-F) polymer oil. The head of oil should not exceed a nominal 6 in. The trap(s) should be placed in a ventilated enclosure that can exhaust any accidentally vented fluorine. If a blowout trap is needed, contact the manufacturer.

All components of fluorine systems using pressures above those protected by blowout traps shall have a rated working pressure above the maximum pressure that could accidentally occur in the system. A safety factor between 5 and 8 shall be used in the system design.

When the maximum fluorine pressure could exceed the rated working pressure of any system component because of the pressure supply source or the heat involved in the operation, the system shall be protected by a spring-loaded pressure-relief device or a rupture disk. When using a pressure-relief device, ensure that device is acceptable for use in a fluorine system. When using a rupture disk, the discharge from the disk shall be directed into a local exhaust ventilation system or extended into an area where it can discharge safely. The Responsible Individual establishes a regular program for replacing rupture disks to prevent corrosion from weakening the disks and causing them to fail prematurely.

Use of a three-disk system is recommended: the inner disk protects the center disk from corrosion by direct contact with gas. The center disk is rated to rupture at a designated pressure, and the outer disk protects the center disk from moisture corrosion.

Valves. All valves for fluorine service shall have dissimilar metal-to-metal seating to prevent galling. They shall be provided with packless stem sealing and Monel or stainless-steel bodies. If packed valves are used, tetrafluoroethylene polymer shall be used in the stuffing box.

Gauges. Gauges with Monel or stainless-steel Bourdon tubes passivated for fluorine service shall be used. Gauges should be appropriate for indicating up to two times the pressures expected at the gauged points in the system.

Hydrogen-Fluoride Traps (Optional). Hydrogen fluoride impurities can be removed from commercial fluorine using a trap containing sodium fluoride.

Flow Meters. Flow meters shall be constructed of materials acceptable for use in a fluorine system.

Purge System. A purge system is required for experiments or operations using fluorine. The purge system shall include an inert gas supply. This gas supply shall be protected from the fluorine system by use of fluorine-compatible check valves.

It may be desirable to treat the fluorine purged from the system rather than release it to the atmosphere. The ES&H Team will determine this need during the design phase of the system and will recommend procedures for treating fluorine exhaust.

Vacuum Pumps. Vacuum pumps compatible with fluorine systems shall be used. To protect the pump, a soda-lime tower followed by a drier shall be included in the vacuum line to pick up trace amounts of fluorine. Vacuum pump systems using liquid nitrogen traps shall have a relief device vented to a local exhaust ventilation system.

Eyewash and Safety Shower Facilities. The Responsible Individual ensures that eyewash and safety shower facilities are located within a 10-sec travel time or 100-ft walking distance of the fluorine operation.

3.2 Administrative Controls

To minimize risks, use only the minimum quantity or concentration required for the operation. This also minimizes the amount of material left over to be disposed of as expensive hazardous waste. Two key administrative controls are OSPs and training. Other controls are also specified in this section.

3.2.1 Safety Plans

The Operational Safety Plan for fluorine operations shall contain the following information:

- The quantity, concentration, and type of material in storage and in use and where it will be stored and used.
- Personal protective equipment (including respirators) to be used.
- Passivation and cleaning procedures (also required in the ESN).
- Safety checklist.
- Procedures for dismantling and disposing of used equipment. Fluoride salts may be in lines and ducts, but they are only modestly toxic and irritating so disposable lab coats and disposable respirators will often offer adequate protection from these salts (but not the gas). Acute exposures of fluoride residues will require whole body coveralls and more protective respirators. Fluorides are environmentally hazardous so fluorides and fluoride-contaminated items shall be disposed of as hazardous waste. Residual fluorine, all fluorine mixtures, or reactive fluoride gases will need to be purged from systems and the fluorine/fluoride sources sealed (shut the valves of cylinders and cap them). Contact the ES&H Team for guidance.

3.2.2 Training

Workers shall have the following training before being allowed to handle fluoride materials:

- HS5030W, "Pressure Safety Orientation"
- HS-5040W, "Intermediate Pressure Safety"
- HS5060W, "Pressure Seminar for Engineers" (for those who prepare engineering safety notes and design the system)
- Review the applicable OSP, Engineering Safety Note and this document.

Personnel who prepare OSPs should take Courses HS0032, "Operational & Facility Safety Plan and Work Procedure Overview," and HS0033, "Preparing Operational & Facility Safety Plans & Work Procedures."

The Hazard Control videotape library also has tapes available on handling fluorine.

3.2.3 Work Practices

Fluorine users shall be aware of and follow these administrative controls:

- Take extra precautions to transport or handle cylinders of pure fluorine, inert gas mixtures containing >10% fluorine, other fluorine mixtures, and oxidizing fluorides because dropping, shocking or striking cylinders could cause an incident.
- Cylinders of fluorine, inert gas mixtures containing >10% fluorine, other fluorine mixtures, and oxidizing fluorides need to be transported in the back of an open truck.
    - — Personnel should not work alone when handling fluorine, including fluorine mixtures. Another person should always be within your sight and earshot, although not necessarily in the immediate area. (See Document 11.2, "Hazards--General and Miscellaneous," in the *ES&H Manual* for details.)
    - — All components to be used in a fluorine system shall be clean and free of organic material and bagged (or otherwise closed off to ensure system cleanliness until final assembly).
    - — All lines and equipment to contain fluorine shall be leak-tested with dry nitrogen or helium before usage.
    - — Repeated bending or excessive vibration of piping or equipment should be avoided. Either can cause the fluorine film that has developed in the system to flake and corrode valves and other system components. Excessive thermal cycling can also cause this problem.

The ES&H Team, industrial hygienist, pressure safety manager, and all other concerned parties shall review procedures and checklists before the system can be initially activated or reactivated after disassembly or modification.

- Systems containing fluorine under pressure shall be inspected for leaks at frequent intervals. If a leak is detected, purge the system immediately and repair the leak. There are three methods to perform the leak test:
    1. Purge fluorine from the system and introduce helium.
    2. Expel ammonia vapor at suspect leak points from a squeeze bottle containing ammonium hydroxide. A white mist will be observed if fluorine is leaking.
    3. Use long metal tongs or forceps to place filter paper moistened with potassium iodide solution near suspected leaks. The paper will turn brown if fluorine is leaking.
- A regular program shall be established for replacing rupture disks when such disks are used in the system.

- The possibility of valves freezing can be minimized as follows:
  - — Never use a regulator or manual control as the on/off control.
  - — When shutting down operations for any extended period, always close the cylinder valve and bleed the pressure in the regulator or manual control to atmospheric pressure.
  - — When the regulator or manual control is removed from the cylinder, replace the metal or plastic cylinder valve outlet cap originally provided.
  - — Use the proper wrench when opening or closing cylinder valves.
  - — Store cylinders in a dry, cool, well-ventilated area.
  - — While the cylinder is in use, rotate the valve stem at least once a day to break up any forming corrosion products.
  - — Use traps or check valves to prevent reverse flow.
  - — Obtain cylinders of a size that will ensure consumption in a short time. Suppliers usually carry a wide range of sizes to meet this need.
  - — Flush the regulator or manual control valve with dry nitrogen or dry inert gas after use.

3.2.4 Gas Monitoring

Gas monitoring is needed where people are or could be present. Contact the area ES&H Team for guidance about available sensors, alarms, and alarm annunciation requirements.

3.2.5 Labels and Signs

Labels, as shown in Fig.1, shall be conspicuously posted near entrances to areas where fluorine is stored or used. Equivalent signs are needed for oxidizing fluorides (contact the ES&H Team to get these signs). In addition to the signs, information concerning the quantity of fluorine in use in the area should be posted at the entrance, along with emergency procedures to be followed in case of an accident. "No Smoking" signs should also be posted where fluorine is stored or used. Lines carrying fluorine shall be labeled once every 20 ft, at wall penetrations, and in concealed spaces. (It's a good idea never to run fluorine lines through concealed spaces!)

All fluorine cylinders shall be barcoded for hazardous material tracking purposes.

3.2.6 Inactive Gas Storage

Containers that are not in use or ready to be used (i.e., cylinders with valves shut, caps on, and thoroughly sealed containers of materials, e.g., XeF_6) shall be stored in protected outdoor locations or dedicated-use buildings for protection against temperature extremes, contact with rain or condensed moisture, and direct sunlight. Indoor storage spaces need to be vented at a rate of 1 cfm/ft^2 or 10 air changes per hour, whichever is

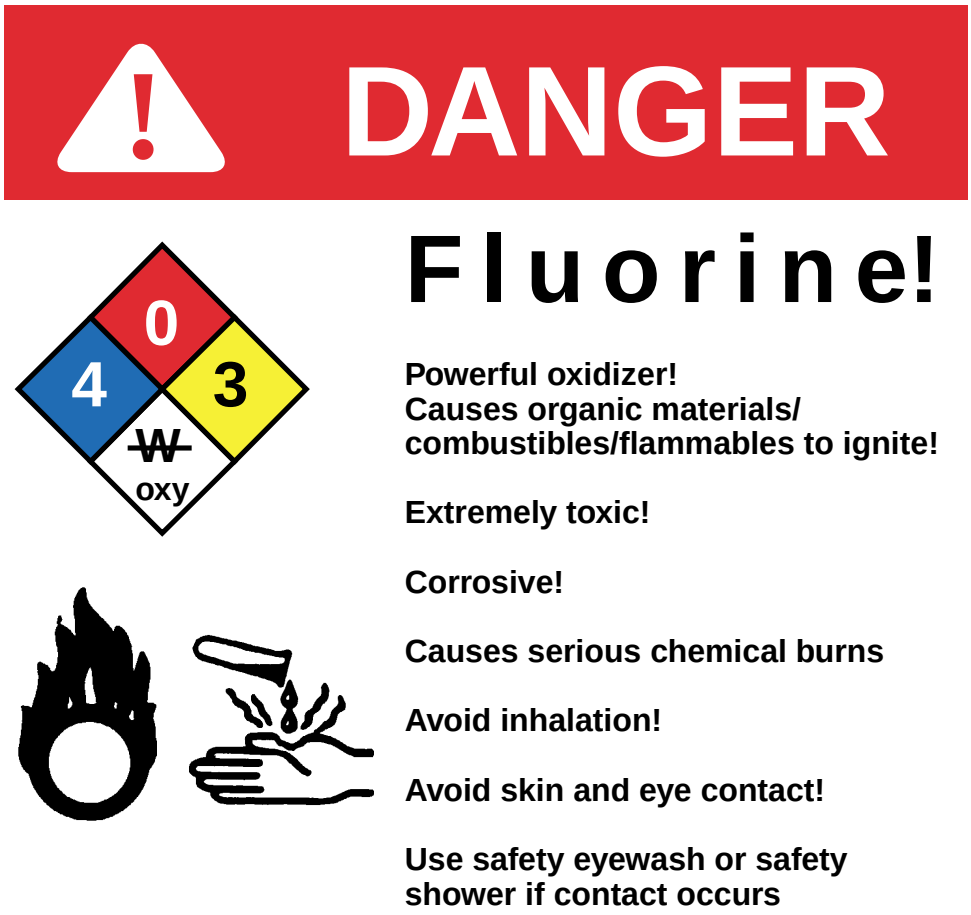

Figure 1. Standard warning for fluorine. It should be conspicuously posted by entrances to where fluorine is stored or used and on the doors of gas storage cabinets. Available from Hazards Control.

greater. These storage areas normally shall be locked and unoccupied and entrances need to be posted with appropriate warning signs. Combustible/flammable materials and reducing agents cannot be stored in the same area.

No part of the cylinders should be subjected to temperatures higher than 52°C (125°F). Therefore, cylinders should be placed away from radiators and other heat sources that could cause an excessive rise in temperature.

Never allow flame to come in contact with any part of a compressed-gas cylinder. Fluorine cylinders are not equipped with pressure-relief devices.

3.2.7 Returning Fluorine Cylinders

Before returning the fluorine cylinders to Industrial Gases, they shall be inspected by the area ES&H Team industrial hygienist or a health and safety technician. Contact Industrial Gases for instructions on returning fluorine cylinders to the vendor/distributor. Do not transport the cylinder to Industrial Gases.

3.2.8 Disposing of Leaking or Damaged Fluorine Cylinders

When you find a leaking or damaged fluorine cylinder, notify the Fire Department immediately (dial 911). They will assess the situation, take action necessary to rescue or protect personnel, and ensure appropriate action is taken to contain the hazard. The Hazards Control Department and Hazardous Waste Management will advise you on how to dispose of a leaking cylinder.

3.2.9 Dismantling Fluorine Systems

Consult the area ES&H Team prior to dismantling a fluorine system. The procedure for dismantling the system shall be documented in the OSP for the experiment or in a special OSP before dismantling can take place.

3.3 Personal Protective Equipment

The PPE required for a fluorine operation shall be detailed on the HAC form and in the OSP. In addition, the worker must know the location of all PPE specified for the operation (including respiratory protective equipment) and the proper use and care of the equipment.

Protective equipment is routinely required in the following situations:

- Wear clean neoprene gloves when directly handling equipment that contains fluorine or has recently contained fluorine.
- Wear neoprene coats and boots to protect the body for short intervals of contact with low-pressure fluorine. This clothing should be designed and worn so that it can be shed immediately.
- Wear safety eyewear at all times. Metal frames are preferable to the customary plastic to eliminate the possibility of the frames catching fire. *Never wear contact lenses when working around fluorine.*
- Wear face shields or goggles, or both, made of chemically resistant polymers whenever you change cylinders or manipulate systems containing fluorine under pressure.

- Special respiratory protective equipment may be needed, depending on the nature of the fluorine system installed and the special circumstances necessitating such equipment. Consult the area ES&H Team for guidance.

4.0 Responsibilities

General responsibilities for all workers are described in Document 2.1, "Laboratory and ES&H Policies, General Worker Responsibilities, and Integrated Safety Management," in the *ES&H Manual*. Specific responsibilities for work involving fluorine and fluorine systems are listed under each title below.

4.1 Workers

- Be familiar with the properties of the chemicals you work with; follow all safety procedures.
- Protect yourself and others in the area from injury in the event the equipment malfunctions or is damaged.
- Report any unsafe or hazardous condition in the area to your work supervisor and the area ES&H Team.

4.2 Responsible Individual

- Prepare the IWS and OSP as specified in Document 2.2, "Managing ES&H for LLNL Work," in the *ES&H Manual*). Prepare the ESN in accordance with Document 18.2.
- Prepare a revised ESN and have it approved when a system handling fluorine, any fluorine mixture, or oxidizing fluoride is changed.
- Arrange to have all unusual experiments involving fluorine peer reviewed in a manner similar to that used for high explosives experiments.
- Order elemental fluorine and all related mixtures in cylinders with CGA 679 connections. Make sure the valve closure torques do not exceed 50 ft-lb (state the closure torque limit in the procurement document).
- Have the area ES&H Team sign all orders before delivering the material to the requestor. Direct deliveries to requestors are not permitted.
- Sign for all shipments received.
- Do not allow incoming shipments to remain in hallways, unoccupied rooms and uncontrolled areas.
- Ensure that calcium -gluconate is available in work areas.

4.3 The Industrial Gas Section of Materiel Distribution

- Notify end user of the arrival of a fluorine cylinder.
- Load list into PARIS and create move ticket.
- CHEMTRACK cylinder.
- Transport to end user in placarded vehicle per HMPTS requirements.
- Scan cylinder to end user, as evidence of delivery.

NOTE: Poison gases cannot be held at the Industrial Gas Facility, Building 518

4.4 Hazards Control Department

- Conduct hazard reviews of proposed, new uses of fluorine and its compounds when requested or as required.
- Assist in the design of safety-related systems and in the preparation and review of OSPs.
- Review ESNs associated with fluorine systems.
- Administer specific courses for fluorine handlers.
- Review the hazard mitigation implementation procedures and the equipment governed by these procedures. Notify the Responsible Individual /lead experimenter of any deficiencies.
- Respond to spills, fires, exposures, or other emergencies involving fluorine and its compounds.
- Review all requisitions for fluorine and its compounds received from the Procurement & Materiel Department in accordance with the requirements in this document.
- Ensure that the Fire Department is equipped to handle fires involving fluorine and its compounds.

4.5 Environmental Protection Department

- Conduct a hazard review to evaluate environmental contamination problems, permit requirements, NEPA declarations, and other environmental issues during the experimental design phase.
- Specify requirements for packaging waste or equipment contaminated with such materials.

- Remove and dispose of packaged waste.
- Properly handle contaminated equipment for disposal.

4.6 Health Services Department

- Specify first-aid requirements for accidental exposures to fluorine and its compounds.
- Maintain appropriate facilities for immediate support of individuals exposed to fluorine and its compounds.

5.0 Work Smart Standards

29 CFR 1910.101, "Compressed Gases General Requirements."

29 CFR 1910.132, "General Requirements" (for personal protective equipment of all kinds).

29 CFR 1910.1200, "Hazard Communication."

29 CFR 1910.1450, "Occupational Exposure to Hazardous Chemicals in Laboratories.

29 CFR 1910, Subpart I, "Personal Protective Equipment."

29 CFR 1910, Subpart J, General Environmental Controls."

29 CFR 1910, Subpart K, "Medical and First Aid."

29 CFR 1910, Subpart M, "Compressed Gas and Air Equipment."

29 CFR 1910, Subpart Z, "Toxic and Hazardous Substances."

40 CRF 262, "Standards Applicable to Generators of Hazardous Waste."

49 CFR 100 -199, "Research and Special Programs Administration, DOT (Off-site)."

ACGIH Industrial Ventilation Manual (23rd edition), 1998.

ACGIH TLVs and BEIs: Threshold Limit Values for Chemical Substances and Physical Agents, 1998.

ANSI B31.1, "Power Piping, ASME Code for Pressure Piping," 1995.

ANSI Z9.5-1992, "American National Standard for Laboratory Ventilation." (see Sections 5.7 and 5.8).

ANSI Z88.2-1992, "Respiratory Protection."

ANSI Z358.1-1990, "American National Standard for Emergency Eyewash and Shower Equipment." (Testing frequency for emergency showers is to be monthly rather than weekly as required by the standards.)

Compressed Gas Association (CGA) Pamphlet S-1.1, *Pressure Relief Device Standards*, Part 1, "Cylinders for Compressed Gases," 1995.

NFPA 45, "Standard on Fire Protection for Laboratories using Chemicals," 1996.

NFPA 55, "Standard for the Storage, Use, and Handling of Compressed and Liquified Gasses in Portable Cylinders."

Public Law 91-596 § 5 (a) (1), OSHA Act of 1970.

UCRL-AR-129189, Rev.1, *LLNL Occupational Medicine Standard: Medical Evaluation of Employees*.

UCRL-AR-128970, Rev. 1, *LLNL Pressure Safety Standard*.

6.0 Resources for More Information

6.1 Contacts

For additional information regarding this document, contact the following:

- Area ES&H Teams
- Industrial Gas Section of Materiel Distribution
- Pressure Safety Manager

6.2 Lessons Learned

Refer to the following Intranet address for lessons learned applicable to the topic discussed in this document:

http://www-r.llnl.gov/llnl_only/es_and_h/lessons/lessons.shtml

6.3 Other Sources

Compressed Gas Association, *Handbook of Compressed Gases*, 3rd edition (1990).

Matheson Gas Products, Inc., *Matheson Gas Data Book* (1990).

Appendix A

Fluorine Emergency Procedures

A.1 Calling for Help

In all accidents involving fluorine, dial 911 for assistance.

A.2 Rescuing the Exposed Victim

Do not attempt to rescue a victim unless you are trained in emergency rescue, are adequately protected from any hazard, and have another trained and equipped person standing by. If you enter a heavily contaminated area, you must wear the PPE to protect skin and use self-contained breathing apparatus or approved airline equipment.

A.3 Treating the Exposed Victim

If That Victim is Someone Else

Skin and Eyes. Remove the victim from the contaminated area as soon as possible. Cleanse the fluorine from skin and eyes by flushing for 15 minutes with copious amounts of water. As you flush, remove any contaminated clothing still there from the victim. Apply calcium gluconate (10%) gel to the exposed skin area only. Do not apply to the eyes.

Inhalation. If you suspect a person has inhaled fluorine, move that person into the fresh air. If that person has stopped breathing, apply mouth-to-mouth resuscitation at once. Also treat the victim for eye and skin exposure by flushing the eyes and skin with large amounts of water. Do not delay emergency treatment; have someone else dial the emergency number.

Refer all affected persons to the Health Services Department, even when the immediate injury seems slight, and give the physician a detailed account of the accident.

If That Victim is You

Skin and Eyes. If your eyes are exposed to fluorine, do not rub them. Flush them with water for at least 20 min, lifting the upper and lower eyelids frequently to ensure complete washing.

If fluorine comes in contact with any part of your body or with your clothing, get into a safety shower immediately and flush your body with large amounts of water for 15 minutes. Thoroughly wash under your nails. Strip off any contaminated clothing as you wash. Apply calcium gluconate (10%) gel to the exposed skin area only. Do not apply to the eyes.

Inhalation. If you have inhaled fluorine, leave the area immediately. Treat yourself for eye and skin exposure by flushing with large amounts of water.

No matter how slight the injury may seem, report it to the Health Services Department immediately, using the Fire Department for transportation. Emergency response personnel will ensure your clothing is washed before returning it to you.

In the Event of Leaks

If fluorine cylinders or equipment leak, evacuate the area immediately and dial 911 for assistance. Ensure no other personnel enter the area until the Fire Department arrives.

In the Event of Fire

Evacuate the area immediately and dial 911 for emergency assistance. Do not attempt to extinguish a fluorine fire. Ensure no other personnel enter the area until emergency response personnel arrive.

Appendix B

Accepted Materials for Fluorine System Components

Table B-1 contains information about materials that are acceptable for use in fluorine systems. It is adapted from a table presented in the *Handbook of Compressed Gases*, 2nd ed. (Compressed Gas Association, Inc., 1981).

When selecting system components for an operation, consult the manufacturer to ensure that those components selected are acceptable for use under the intended temperatures and pressures. At high temperatures, nickel or Monel is the material of choice. Teflon is the preferred gasket material. Air Force Manual 161.30, Volume II, has useful information about halogenated halides.

Table B-1. Acceptable materials for fluorine systems.

System component	Gaseous operation, normal temp	Liquid operation, low temp
Lines and fittings	**Nickel** **Monel[a]** **Copper[b]** **Brass** **Stainless steel 304L** **Aluminum 2017, 2024, 5052, 6061** **Mild steel (low pressure)**	**Monel** **Stainless steel 304L** **Copper** **Aluminum 2017, 2024, 2050**
Storage tanks	**Stainless steel 304L** **Aluminum 6061** **Mild steel (low pressure)**	**Monel** **Stainless steel 304L** **Aluminum 6061**
Valve bodies	**Stainless steel 304** **Bronze** **Brass**	**Monel** **Stainless steel 304** **Bronze**
Valve seats	**Copper** **Aluminum 1100** **Stainless steel 303** **Brass** **Monel[a]**	**Copper** **Aluminum 1100** **Monel**
Valve plugs	**Stainless steel 304** **Monel[a]**	**Stainless steel 304** **Monel**
Valve packing	**Tetrafluoroethylene polymer**	**Tetrafluoroethylene polymer**
Valve bellows	**Stainless steel, 300 series** **Monel[a]** **Bronze**	**Stainless steel, 300 series** **Monel** **Bronze**

Table B-1. Acceptable materials for fluorine systems. (cont'd)

System component	Gaseous operation, normal temp	Liquid operation, low temp
Gaskets	**Aluminum 1100** **Lead** **Copper** **Tin** **Tetrafluoroethylene polymer** **Red rubber (5 psig)** **Neoprene (5 psig)** **Kalrez[c]**	**Aluminum 1100** **Copper**

[a] Monel is the material of choice for ≥10% F_2 mixtures or dilute F_2 at elevated temperatures and pressures.

[b] Stainless steel and copper tubing with TFE Teflon, FEL, or KEL-F may be used with 5% F_2 mixtures at room temperature.

[c] Kalrez is the material of choice for 5% F_2 mixtures.

Appendix C

Fluorine System Cleaning and Passivation Procedures

C.1 System Cleaning

System cleanliness and passivation are critical to the successful handling of fluorine. All equipment, lines, and fittings intended for fluorine service shall be leak-tight, dry, and thoroughly cleansed of all foreign matter before use. Following are *minimal* guidelines for system cleaning. Experimental requirements may dictate a more thorough procedure, particularly for pure fluorine and reactive fluorides.

1. Wash and rinse thoroughly with hot water. Do not allow to dry.
2. Rinse with acetone.
3. Degrease with Oakite solution (1 cup of Oakite diluted with 3 gallons of deionized water).
4. For polymers (Teflon or Kalrez), squirt Oakite solution onto a clean, lint-free wipe and then wipe the polymer clean.
5. Dry with clean, oil-free, dry air or nitrogen, or in a vacuum oven.
6. Assemble system and check for leaks at working pressure with an inert gas. A vacuum check is also desirable.
7. Evacuate the system to 4–5 μm or less and at the same time heat to at least 120°C, or 10–20°C above operating temperature. Hold for 1 h after base pressure is obtained.

Documentation that the system has been cleaned to at least these guidelines shall be maintained by the responsible individual/designer.

C.2 Passivation

The corrosion resistance of all materials used with fluorine depends upon the passivation of the system. This operation is intended to remove the last traces of foreign matter from the system and to form a passive fluoride film on the metal surface. At room temperatures, fluorine reacts vigorously with most metals to form this protective fluoride film; however, further reaction may be obtained by raising the temperature. For this reason, passivation shall be accomplished at the working temperature and pressure of the system or a few degrees higher. Using the standard regulator manifold as an example, the following can serve as a guideline to system passivation.

The procedure outlined below may be used for passivation with dilute fluorine mixtures.

CAUTION

Dropping, striking, or shocking the fluorine cylinders may result in an exposure incident.

1. Wear protective gear: safety goggles, full-face shield, flame-retardant gloves, and apron. A second person should be present.
2. Make sure the vent blower system is operating. Ensure the active fluorine detector is operating, if applicable.
3. Make a careful visual inspection of the exterior of the cylinder, valve, and CGA connection. Check for corrosion or mechanical problems. Verify the cylinder pressure tag at 500 psi or less.
4. Check the tightness of the packing nut—should be 40 ft-lb, nominally right-hand thread.
5. Slowly loosen the outlet cap.

CAUTION

A cross-seat leak may have pressurized the outlet.

6. Check the valve outlet and system inlet for foreign material (solid or liquid).

CAUTION

Two connections are in general use in the fluorine industry: CGA670 and CGA679. Make certain that you have a match between the standard regulator manifold and the supply valve outlet.

7. Install a new gasket (degreased, dried, and lint free).
8. Make sure that the air-operated valve is closed and the regulator on the manifold is backed out.
9. Attach the cylinder to the regulator manifold.
10. Clamp the cylinder to prevent torque from being applied to the regulator manifold upon opening the valve.

Attach a remote cylinder valve handle and close the barricade.

Remote temperature and pressure monitoring capabilities are desirable during the passivation process because pressure surges and rapid temperature rises are indicative of possible system failure.

1. Check the supply cylinder and upstream connections to the regulator for leaks at 500 psig with an inert gas source. Check the downstream connections for leaks at the working pressure.
2. Vent and evacuate the leak-check gas.
3. Close all valves and back off the regulator.
4. Open the fluorine-supply cylinder valve as gently as possible and close it immediately. Monitor the temperature in the exposed region.
5. After 10 min or when the temperature is ambient, open the air-operated valve. Note the pressure and monitor the temperature in the newly exposed region.
6. After 10 min or when the temperature is ambient, set the regulator to 5 psig. Note the pressure drop on the supply gage and monitor the temperature in the newly exposed regions. Back off the regulator and monitor the 100-psi gage.
7. After 5 min or when the temperature and pressure are stable, set the regulator to 5 psig. The user may start passivating the system by opening the system valve on the regulator manifold. The user shall follow the guidelines of slowly exposing sections of the system to increasing concentrations of fluorine until working conditions are achieved.
8. When the supply gage indicates approximately 50 psig, back off the regulator. Open the vent valve and vent the system to atmospheric pressure. Close the vent valve.
9. Gently open and immediately close the fluorine-supply valve. The supply gage should read the approximate cylinder pressure. Monitor the temperature and pressure as before.
10. After 5 min or when the temperature and pressure are stable, set the regulator to 10 psig.
11. After 5 min or when the temperature and pressure arc stable, set the regulator to 15 psig. Monitor the temperature and pressure.
12. After 5 min or when the temperature and pressure are stable, set the regulator to 20 psig. Monitor the temperature and pressure
13. Back off the regulator. Vent the downstream system to atmospheric pressure. Close the vent valve.
14. Gently open the fluorine-supply valve. The supply gage should read the cylinder pressure.

15. Set the regulator to 10 psig. Wait 5 min or until the temperature and pressure are stable.

    Set the regulator to 20 psig. Wait 5 min or until the temperature and pressure are stable.

    Set the regulator to 30 psig. Wait 5 min or until the temperature and pressure are stable.

16. The manifold is now passivated for 30-psig maximum operating pressure and room temperature conditions.

17. If higher operating temperatures are to be used, repeat steps 8 through 16 at 25–50°C intervals.

Avoid vibration and bending of passivated surfaces. This may cause flaking or spalling of the fluoride film, exposing unpassivated surfaces and fouling valve seats. Avoid exposing system to air, or any gas containing water or organic materials.

Systems may also be passivated with pure fluorine by a slow and gradual exposure to increasing concentrations. Much smaller pressure increases shall be used in conjunction with greater pressure measurement resolution. For example:

Vacuum of 1 μm or less	Hold for 15 min.
1 μm to 0.1 atm	Hold for 15 min or until the temperature and pressure stabilize.
0.1–0.3 atm	Hold for 15 min or until the temperature and pressure stabilize.
0.3–0.6 atm	Hold for 15 min or until the temperature and pressure stabilize.
0.6–1.0 atm	Hold for 30 min or until the temperature and pressure stabilize.
1.0–5.0 atm	Hold for 30 min or until the temperature and pressure stabilize.

All increases shall be added slowly. The supply source shall be valved out of the system between additions (to minimize the available fluorine if the reaction goes out of control). If operating temperatures are to be above room temperatures, repeat the above procedure at 25–50°C intervals to 10–20°C above the operating temperature.